Evaluation of Molybdenum−Sulfur Interactions in Molybdoenzyme Model Complexes by Gas-Phase Photoelectron Spectroscopy. The "Electronic Buffer" Effect

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Abstract: The first ionization energy in the gas-phase photoelectron spectra (PES) of Tp*Mo(E)(tdt) complexes (where E = O, S, NO; Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; tdt = 3,4-toluenedithiolate) is essentially independent of the nature of E, even though the formal oxidation state of the Mo center ranges from +2 to +5. The PES data for the tdt complexes contrast with the results for analogous complexes with alkoxide ligands, which show large variations in first ionization energy (Westcott, B. L.; Enemark, J. H. *Inorg. Chem.* **1997**, *36*, 5404−5405). For the tdt complexes the relative intensities of the two lowest energy ionizations do not substantially change as the excitation source is varied among Ne I, He I, and He II radiation, even though the atomic photoionization cross sections for Mo 4d and S 3p orbitals change dramatically over this energy region. These results all point to substantial covalency in the Mo−S bonds. It is proposed that the S atoms of the tdt ligand act as an "electronic buffer" to the effects of strongly bound axial ligands, and that this is an important role of ene-dithiolate (dithiolene) coordination in the molybdenum centers of enzymes.

Introduction

A common structural feature[1,2] of the large group of molybdenum-containing enzymes that catalyze a wide range of oxidation/reduction reactions in carbon, sulfur, and nitrogen metabolism[3] is coordination by the sulfur atoms of one (or two) unique ene-dithiolate[4] ligand derived from the side chain of a novel substituted pterin (molybdopterin).[5] For example, the recent crystal structure of chicken liver sulfite oxidase[6] shows approximate square-pyramidal geometry about the molybdenum atom, which is coordinated by two sulfur atoms from one ene-dithiolate ligand, a cysteinyl sulfur, a terminal oxo group, and a water (or hydroxide) ligand, as depicted schematically in Figure 1.

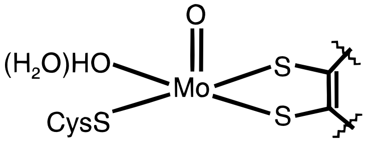

Figure 1. Schematic view of the coordination of the molybdenum center in chicken liver sulfite oxidase as determined from the protein crystal structure.[6]

The interest in interactions between transition metal centers and sulfur is not limited to metalloenzymes. Such complexes have shown wide utility in such areas as catalysis,[7] superconductivity,[8] semiconductivity,[9] and intercalation reactions.[10] Molybdenum complexes in particular have shown a rich and diverse chemistry when sulfur donors are involved. Internal electron-transfer processes in Mo−S complexes allow for synthetically useful redox reactions and illustrate the small energy gap between S 3p and Mo 4d orbitals.[11]

The importance of molybdosulfur complexes in biological and industrial catalysis has led to the study of a wide range of monomeric,[12] dimeric,[13] and cluster complexes.[14] Complexes with sulfur donation to the Mo center often exhibit different spectroscopic behavior from those with alkoxide donors.[15] It has been suggested that one role of the ene-dithiolate coordination in molybdoenzymes is to buffer the influence of strong π ligands.[16]

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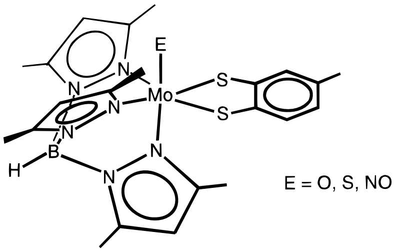
This study uses gas-phase ultraviolet photoelectron spectroscopy (PES) to evaluate the effects of ene-dithiolate coordination upon the electronic structure of molybdenum model complexes **1** of the general formula Tp*MoE(tdt), where Tp* is hydrotris(3,5-dimethyl-1-pyrazolyl)borate, E is O, S, or NO, and tdt is 3,4-toluenedithiolate. These complexes are very similar structurally, and those with E = O have EPR parameters that are similar to those for the molybdenum center of sulfite oxidase.[17] In addition, Tp*MoO(tdt) possesses the basic structural core of a terminal oxo group cis to a 1,2-dithiolate, as has been found for sulfite oxidase (Figure 1).[6] One impetus for these PES studies of **1** was the evidence for substantial Mo−S covalency in Tp*MoO(tdt) from MCD[18] and EPR studies.[17] Gas-phase PES is a powerful tool for probing metal ligand covalency in isolated molecules because the relative ionization intensities observed in a PE spectrum are dependent upon the incident photon energy.[19] Thus, for complexes **1**, comparison of the photoelectron spectra obtained with different energy ionization sources should provide insight concerning the amount of molybdenum and sulfur character in the valence orbitals from which the ionizations arise.



We have also recently communicated the gas-phase He I PES of complexes of the type Tp*MoE(OR)$_2$.[20] For the alkoxide complexes, the formally Mo(II) nitrosyl complexes were found to be 0.8 eV *more difficult* to ionize than the formally Mo(V) oxo analogues. This counterintuitive behavior was attributed to the strong π-accepting ability of the NO ligand and agrees with a theoretical study.[21] In contrast to the alkoxide complexes, the first ionization energies of the Tp*MoE(tdt) complexes (**1**) discussed here are *essentially independent* of the nature of E, even though the formal oxidation state of the Mo center in these complexes ranges from +2 to +5. These results corroborate our earlier studies[17,18] that indicate substantial covalency in the Mo−S bonds, and underscore the important electronic role of ene-dithiolate coordination to the molybdenum center of enzymes.

Experimental Section

Compounds. Samples of Tp*MoO(tdt) and Tp*Mo(NO)(tdt) were prepared by published procedures;[22,23] Tp*MoS(tdt) was kindly provided by Dr. C. G. Young of the University of Melbourne.

Data Collection. Photoelectron spectra were recorded with use of an instrument that features a 36-cm hemispherical analyzer (McPherson) and custom designed sample cells and detection and control electronics.[24] The excitation source was a quartz lamp with the ability, depending on operating conditions, to produce Ne I (16.85 eV), He I (21.21 eV), or He II (40.8 eV) photons. For the He I and He II experiments, the ionization energy scale was calibrated by using the $^2E_{1/2}$ ionization of methyl iodide (9.538 eV), with the argon $^2P_{3/2}$ ionization (15.759 eV) used as an internal energy scale lock during data collection. For Ne I experiments, the Xe $^2P_{3/2}$ ionization (12.130 eV) was used as the internal energy scale lock. During He I and He II data collection the instrument resolution, measured by using the full-width-at-half-maximum of the argon $^2P_{3/2}$ ionization, was 0.015−0.025 eV. During Ne I data collection the instrument resolution, measured by using the full-width-at-half-maximum of the xenon $^2P_{3/2}$ ionization, was 0.012−0.020 eV. All data are intensity corrected with an experimentally determined instrument analyzer sensitivity function that assumes a linear dependence of analyzer transmission (intensity) to the kinetic energy of the electrons within the energy range of these experiments.

All of the spectra were corrected for the presence of ionizations from other lines. These corrections are necessary because discharge sources are not monochromatic.[25] The He I spectra were corrected for the He Iβ line (1.9 eV higher in energy, and 3% the intensity of the He Iα line), the He II spectra were corrected for the He IIβ line (7.568 eV higher in energy, and 12% the intensity of the He IIα line), and the Ne I spectra were corrected for spin−orbit splitting of the Ne I line, which produces a line 0.18 eV lower in energy and 15% the intensity of the main Ne I line.

All samples sublimed cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue. The sublimation temperatures (in °C, at 10^{-4} Torr) were as follows: Tp*MoO(tdt), 202−218; Tp*MoNO(tdt), 220−229; Tp*MoS(tdt) 216−231 (monitored using a "K" type thermocouple passed through a vacuum feedthrough and attached directly to the ionization cell).

Data Analysis. In the figures of the data, the vertical length of each data mark represents the experimental variance of that point.[26] The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks.[26] The bands are defined with the position, amplitude, half-width for the high binding energy side of the peak, and half-width for the low binding energy side of the peak. The peak positions and half-widths are reproducible to about ± 0.02 eV ($\approx 3\sigma$ level). For the different compounds studied, the Ne I spectrum was fit first, where the number of peaks used in the fit was based on the features of the band profile and the number of peaks necessary for a statistically good fit. The Ne I fit was then used to fit the spectra from the other sources. For the He I and He II fits, the peak positions and half-widths were fixed to those of the Ne I fit, with only the peak amplitudes allowed to vary to account for the changes in photoionization cross section as the source energy is varied (vide infra).

Confidence limits for the relative integrated peak areas are about 5%, with the primary source of uncertainty being the determination of the baseline, which is caused by electron scattering and taken to be linear over the small energy range of these spectra. The total area under a series of overlapping peaks is known with the same confidence, but the individual peak areas are more uncertain. The fitting procedures used are described in more detail elsewhere.[26]

Results and Discussion

General Assignment of Spectra. The He I photoelectron spectra from 10.5 to 6.5 eV of the three ene-dithiolate complexes are shown in Figure 2. In this region, the ionizations located from about 8 to 10.5 eV arise from the removal of electrons from orbitals primarily associated with the Tp* and E ligands. The large number of individual ionizations and the overlapping nature of these bands make it exceedingly difficult to unambiguously assign any feature in this region to a particular ionization.

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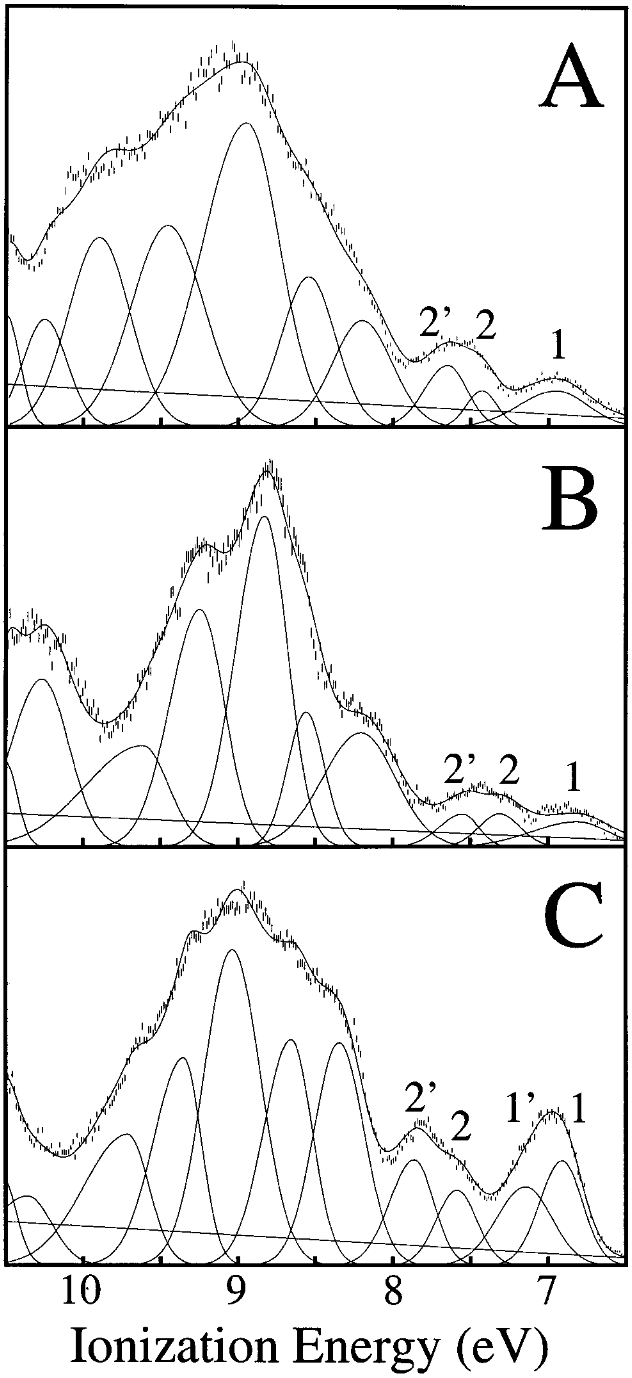

Figure 2. He I photoelectron spectra of (A) Tp*MoO(tdt), (B) Tp*MoS(tdt), and (C) Tp*MoNO(tdt).

Table 1. Comparison of First Ionization Potentials for Ene-Dithiolate and Alkoxide Complexes

complex	first I.P. (eV, ±0.02)	ref
Tp*MoO(OEt)$_2$	6.57	20
Tp*Mo(NO)(OEt)$_2$	7.40	20
Tp*MoO(tdt)	6.95	this work
Tp*MoS(tdt)	6.88	this work
Tp*Mo(NO)(tdt)	6.90	this work

Table 2. Comparison of Relative Areas of Ionizations 1 and 2 for Ene-Dithiolate Complexes

complex	ionization	relative area (±5%)		
		Ne I	He I	He II
Tp*MoO(tdt)	1	1.00	1.00	1.00
	2 + 2′	1.44	1.53	1.24
Tp*MoS(tdt)	1	1.00	1.00	
	2 + 2′	1.12	1.39	
Tp*Mo(NO)(tdt)	1 + 1′	1.00	1.00	1.00
	2 + 2′	0.88	0.88	1.25

The ionizations of primary interest for Mo−S covalency are those located below 8 eV. For the oxo and sulfido complexes, the ionization band located at about 6.8 eV and labeled ionization 1 in Figure 2, spectra A and B, has a very similar shape to the ionization in the PES of the analogous alkoxide complexes that has been attributed to the ionization of the Mo d^1 electron from these formally Mo(V) complexes.[20] For the nitrosyl complex, the first ionization feature that is fit with two Gaussians and labeled 1 and 1′ in Figure 2C is also very similar in appearance to the ionization band in the spectra of the analogous alkoxide complex that has been assigned to ionization from the two nearly degenerate, primarily metal-based orbitals of the formally Mo(II) center.[20] For all three of these complexes there is an ionization band located between about 7.25 and 8 eV that has no counterpart in the spectra of the analogous alkoxide complexes. These ionization bands, labeled 2 and 2′ in Figure 2, are reasonably assigned to primarily sulfur-based orbitals. However, in making this preliminary assignment of the primary atomic character of the orbitals from which these ionizations arise, it must be remembered that contributions from other atoms in the molecule are also mixed into these orbitals. This mixing is of particular importance for understanding the electronic structure of these complexes (vide infra).

Comparison of First Ionization Energies. The first ionization energies measured for the ene-dithiolate complexes and the alkoxide complexes previously reported are listed in Table 1. Comparison of the ionization energy shifts observed between related molecules as substituents or ligands are changed gives an indication of the types of electronic interactions that predominate within a molecule. In a series of metal complexes, as a ligand is changed, particular ionizations will be affected by two separate interactions.[27] The first of these is a charge effect, which will shift ionizations as the charge potential felt in a particular orbital is changed due to differences in formal oxidation state of a metal and the electronegativity of the ligand. The second is an overlap effect, which causes ionizations to be shifted as the orbital from which the ionization arises is stabilized or destabilized due to different amounts of bonding interactions with the ligands.

For the Tp*MoE(OR)$_2$ complexes, the first ionization potential of the oxo complex is 6.57 ± 0.02 eV, while the first ionization potential of the nitrosyl complex is 7.40 ± 0.02 eV.[20] The oxo complex is formally Mo(V), whereas the nitrosyl complex is formally Mo(II). Formal oxidation state arguments would predict that the Mo(V) oxo complex should be more difficult to ionize than the Mo(II) nitrosyl complex. However, the opposite behavior is observed; the formally d^1 Mo(V) oxo complex is 0.83 eV easier to ionize than the formally d^4 Mo(II) complex. The effect from the charge shift is expected to destabilize the ionization for the Mo(II) complex as compared to the Mo(V) complex, but the overlap difference between the strong π-accepting nitrosyl ligand and the π-donating oxo ligand counteracts the charge shift, leading to the overall effect that the first ionization of the Mo(II) nitrosyl complex is stabilized with respect to the first ionization of the Mo(V) oxo complex.

The first ionization potential of Tp*MoO(tdt) is 6.95 ± 0.02 eV, 0.38 eV higher than that for Tp*MoO(OEt)$_2$. This suggests

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that the ene-dithiolate ligand has a significant stabilizing effect on the metal center as compared to the alkoxide ligands. The first ionization potential for Tp*MoS(tdt) is 6.88 ± 0.02 eV, similar to the first ionization potential of Tp*MoO(tdt), as would be expected for another formally Mo(V) complex.

The complex Tp*MoNO(tdt) has a first ionization energy of 6.90 ± 0.02 eV, essentially the same energy measured for Tp*MoO(tdt) and Tp*MoS(tdt). This is in striking contrast to the behavior of the first ionization energies for the alkoxide complexes.[20] As described earlier, for the alkoxide complexes the π-overlap effect dictates the first ionization energy of the complexes. For the ene-dithiolate complexes, however, the sulfur ligation controls the position of the first ionization, essentially neutralizing the effects of both formal oxidation state change at the metal center and the presence of the strong π-axial ligand.

The control that the ene-dithiolate ligand has upon the first ionization energy of these complexes illustrates the importance of this moiety to the reactivity found for molybdoenzymes. The ene-dithiolate ligand acts as an "electronic buffer", effectively dampening the harsh electronic changes that would otherwise be expected to take place at the active site in these enzymes as metal formal oxidation state changes and atom transfer reactions occur.

Comparison of Ionization Intensity Changes. The He I PES of the three ene-dithiolate complexes that were discussed in the previous section indicate that bonding interactions between the Mo atom and the sulfur ligands dominate the electronic structures of these complexes. Other spectroscopic studies have also indicated that a large amount of covalency is present in the molybdenum−sulfur bonding in these complexes.[17,18] The amount of mixing of molybdenum and sulfur character in the frontier orbitals of these complexes can also be evaluated via PES by investigating the variation in the intensities of the ionizations as a function of the incident photon energy, because the intensity of ionization bands is related to the atomic character of the orbital from which the ionizations arise. The amount of mixing of molybdenum and sulfur character in the valence orbitals was evaluated by collecting PE spectra with He II and Ne I ionization sources in addition to the spectra of Figure 2 that were collected with a He I ionization source.

After corrections for instrument resolution and sensitivity, and for other excitation lines in the sources, photoelectron spectra obtained with different ionization sources differ only in the relative intensities of the ionization bands. This difference is primarily due to the different inherent photoionization cross-sections of atomic orbitals, which vary as the incident photon energy changes. From theoretical estimates,[28] the photoionization cross section of Mo 4d orbitals increases by a factor of 2 as compared to S 3p orbitals when comparing spectra from He II and He I sources, while the photoionization cross-section of Mo 4d orbitals decreases by a factor of 4 as compared to S 3p orbitals when comparing spectra from Ne I and He I sources. Comparison of He I and He II spectra to these theoretical cross sections has been shown to be very useful in the assignment of the photoelectron spectra of many transition metal complexes.[29] We have also evaluated the Ne I spectra of several sulfur- and metal-containing compounds and have found that the general trends predicted by the theoretical Ne I photoionization cross-sections are accurate, indicating that any additional influences to the intensity of ionizations from autoionization or resonance are insignificant.[30] These atomic photoionization cross-sections indicate that if the ionizations labeled 1 arise from orbitals that are primarily molybdenum in character, and the ionizations labeled 2 arise from orbitals that are primarily sulfur in character, then the relative intensities of these two ionization bands should change dramatically when the Ne I, He I, and He II spectra of each complex are compared.

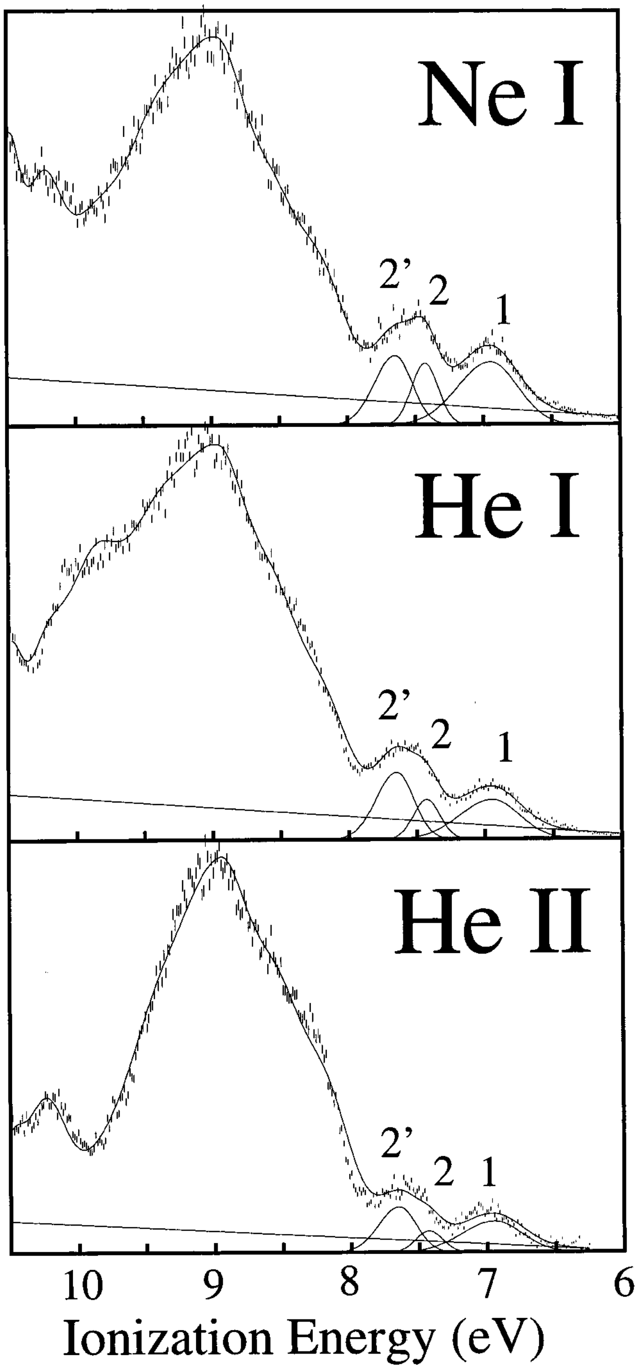

Figure 3. Ne I, He I, and He II photoelectron spectra of Tp*MoO(tdt).

The spectra of Tp*MoO(tdt) collected when the three different ionization sources are used are shown in Figure 3; the spectra of Tp*MoS(tdt) collected when He I and Ne I sources are used are shown in Figure 4; and the spectra of Tp*MoNO(tdt) collected when the three different ionization sources are used are shown in Figure 5. The relative areas of the ionizations labeled 1 and 2 for each complex are also given in Table 1. As

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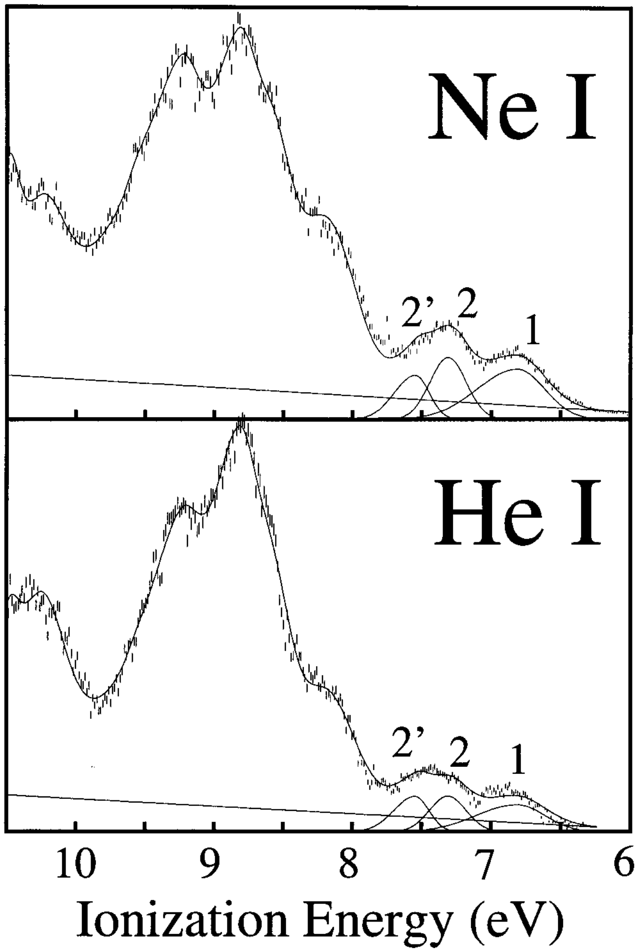

Figure 4. Ne I, He I, and He II photoelectron spectra of Tp*MoS(tdt).

can be clearly seen from the spectra for each complex, no dramatic changes in the relative intensities of ionizations 1 and 2 take place as the incident photon energy is changed. The changes that are observed are only slightly greater than the error of the measurement, and therefore imply that ionizations 1 and 2 originate from molecular orbitals that have nearly equal molybdenum and sulfur character.

Conclusions

The PES of the Tp*MoE(tdt) complexes reported here strongly suggest that the interaction of the Mo center with the sulfur chelate dominates the ground-state electronic structures of the complexes. The similarity of the first ionization energy for all three Tp*MoE(tdt) complexes indicates that the changes in formal oxidation state of the metal and the π effects of the strongly bound axial ligand are essentially neutralized by the coordinated ene-dithiolate ligand. The variable energy PES of Tp*MoO(tdt) shows that this observed electronic buffering effect is due to substantial covalency of the Mo−S bonds, and this conclusion is corroborated by other spectroscopic studies of these complexes.[17,18] These results are in agreement with the general expectation that Mo−S bonds in biology are highly covalent. Here we have demonstrated experimentally the dramatic effect that a large amount of Mo−S covalency has upon the electronic structures of these Tp*MoE(tdt) complexes. These PES results provide direct experimental evidence that coordination of the ene-dithiolate unit alone is sufficient to "electronically buffer" the metal center, and we propose that this is a primary role for ene-dithiolate coordination in molybdoenzymes.

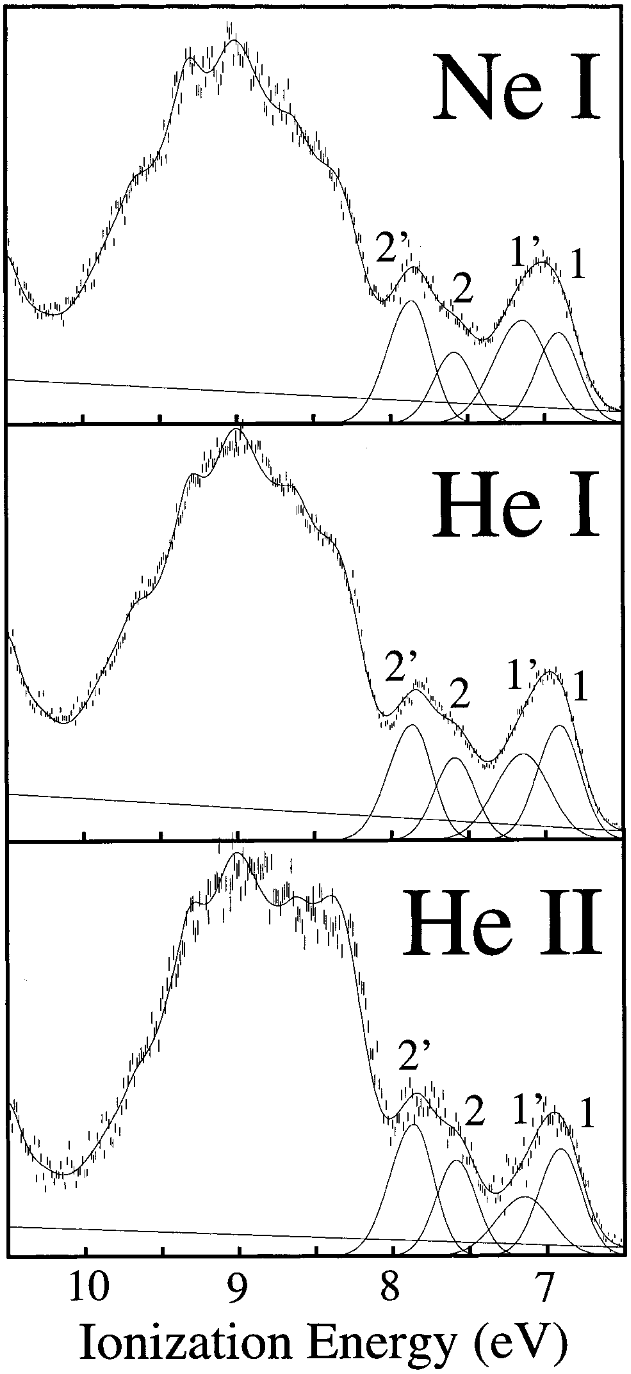

Figure 5. Ne I, He I, and He II photoelectron spectra of Tp*MoNO(tdt).

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